Model Reduction for Chemical Kinetics An Optimization Approach [*]

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Abstract

In this preliminary report we describe an optimization-based approach for reduction of the number of reactions in chemical kinetics models. Numerical results for several reaction mechanisms are given, and future plans are outlined.

1 Introduction

The kinetics of a detailed chemically reacting system can potentially be very complex. Although the chemist may be interested in only a few species, the reaction model almost always involves a much larger number of species. Some of those species are referred to as radicals. These are very reactive species (usually of low concentration) which can be important intermediaries in the reaction scheme. A large number of elementary reactions can occur among the species; some of these reactions are fast and some are slow. The aim of simplified kinetics modeling is to derive the simplest reaction system which retains the essential features of the full system.

The conventional technique [26, 20, 21] is to systematically apply the so-called steady-state approximation to the appropriate radicals, the partial-equilibrium approximation to the fast reactions, and to ignore the very slow (and therefore unimportant) reactions. The investigator is responsible for identifying the appropriate radicals, the fast elementary reactions and the very slow ones, by making intelligent

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order of magnitude estimates using information gathered from detailed examination of available data. A skilled and knowledgeable chemical kineticist is usually needed, and the results obtained are expected to be valid only in some limited domain of initial and operating conditions, for a limited interval of time. Usually the obtained reactions are not elementary reactions and actually represent groups of reactions lumped together. This makes the reduced model more accurate, but the physical meaning of the elementary reactions may be lost.

Sensitivity analysis has often been used for the purpose of obtaining information to develop a reduced order mechanism. In many cases, this approach has been successful [24, 9, 5]. However for some systems, sensitivity analysis may be misleading. Defining as parameters the rate constants of the chemical reactions, sensitivity analysis determines the change in the species concentration for small perturbations of the rate constants. If a reaction is slow and unimportant, it can be identified in this way. However, sensitivity analysis may also single out fast reactions which are important and therefore should not be deleted. To see how this can happen, consider for example determining the sensitivity with respect to perturbation of the parameters λ_1, λ_2, of the following linear stiff differential equation

$$y' = (\lambda_1 + \lambda_2)y - (\lambda_1 + \lambda_2)\left(f(t) + \frac{g(t)}{\lambda_2}\right) + \frac{g'(t)}{\lambda_2} + f'(t), \quad y(0) = \frac{g(0)}{\lambda_2} + f(0) \quad (1)$$

where $|\lambda_1|, |\lambda_2| >> 0$. This problem has solution $y = f(t) + g(t)/\lambda_2$. Let $s_i = dy/d\lambda_i, i = 1, 2$. Then the sensitivities satisfy

$$\begin{aligned} s_1' &= (\lambda_1 + \lambda_2)s_1 + \left(y - \left(f(t) + \frac{g(t)}{\lambda_2}\right)\right), \quad s_1(0) = 0 \\ s_2' &= (\lambda_1 + \lambda_2)s_1 + \left(y - \left(f(t) + \frac{g(t)}{\lambda_2}\right)\right) + \frac{(\lambda_1 + \lambda_2)g(t)}{\lambda_2^2} - \frac{g'(t)}{\lambda_2^2}, \quad s_2(0) = -\frac{g(0)}{\lambda_2^2}. \end{aligned}$$

Let $\lambda_1 = -1000$, $\lambda_2 = +10$. The solution for s_1 is $s_1 = 0$. If the term (reaction) corresponding to λ_1 is deleted from the original system, the reduced system will be unstable. We note that sensitivity is not giving the ‘wrong answer’ in this example. Instead, it is giving the correct answer but to the wrong question. Sensitivity tells us the change in the solution corresponding to a small change in the parameter. By deleting the term corresponding to λ_1, we are making a large change in that parameter. Also, sensitivity tells us only the change in the solution to the original system corresponding to a small change in the parameter. It may not yield enough information about the sensitivity of neighboring solutions with respect to the parameter to guarantee stability of the reduced system. See also [1, 6].

The problem of obtaining a reduced model for the chemical kinetics problem has been considered by a number of authors. In an interesting series of papers [17, 16], Lam et al. have proposed the Computational Singular Perturbation (CSP) method for automatically determining appropriate simplified kinetics models. The CSP method identifies the fast and slow modes as the system advances in time. The reduced order model at any given time is solvable by explicit time-stepping methods because the fast modes have been identified and approximated by algebraic constraints, leaving only the slower modes in the differential system.

Another approach has recently been taken by Maas and Pope [19]: the slow manifold approach. The aim is to find a reduced system with a much smaller number of variables and equations than the original system. If it is possible to describe a system with a very small number of variables, then one can use a table look-up scheme to model the chemistry in complicated combustion processes like turbulence. The method employs an analysis of the eigenvalues and eigenvectors of a local linearized system to identify the fast and slow modes and obtain a reduced system. In contrast to other reduced mechanisms, this method does not provide simple or closed-form expressions for the chemical kinetics. Thus it is primarily useful in the context of table-lookup as described above.

Yet another method is described by Vajda, Valko and Turanyi [25]. This method also employs an eigenvalue-eigenvector analysis of the local linear problem.

A great deal of work has been done on developing reduced-order models for linear differential systems, see [12, 13] and the references therein. These methods also proceed by identifying the large modes and constructing a reduced order model based on the subspace defined by these large modes. Stability of the reduced-order model is an important consideration.

Chemical mechanisms are sufficiently nonlinear that a global approach may be warranted. When nonlinear effects are important, with current methods based on a linear methodology, it is up to the chemist to be alert to the possibility of secondary nonlinear effects in the mechanism leading to parameter interactions, and to uncover their causes on the basis of available chemical knowledge [25]. Methods based on local linear analysis can be helpful in pointing out a potential problem, but it still requires a chemist to solve it. This report describes our work to develop a global, nonlinear approach which has the potential to automatically find a reduced-order mechanism which inherits the stability and captures the nonlinear behavior of the original system in the regime of interest, with a system of equations which has some physical relevance and interpretation and which would usually need to change only a few times during the course of a given problem.

2 Principles of the new algorithm

Our objective has been to develop a numerical method for model reduction of chemical kinetics which could produce a reduced model with the following properties:

1. The reduced-order model accurately models those properties of the original system which are of interest, over the given problem domain.

2. The reduced-order model inherits the stability properties of the original system.
3. The reduced-order model is simpler and much cheaper to evaluate than the original system.
4. Nonlinear behavior should be preserved by the reduced-order model.
5. The reduced-order model makes physical sense and potentially offers some physical insight.

We expect to be able to use this reduced order model over a range of operating conditions which are nearby to the conditions for which it is developed. It is not reasonable for this class of problems to seek a reduced order model which is valid over all possible operating conditions. To see why this is true, consider for example chemical kinetics at two very different temperatures. Then it may be that a completely different set of reactions is important in the two systems.

Given n chemical species y_i and N reactions $F_i(y)$, the original ODE system is given by

$$y' = g(y) = \sum_{r=1}^{N} S_r F_r(y), \tag{2}$$

where $S_r \in \Re^n$ are the stoichiometric coefficients for reaction F_r. Typically $N >> n$ because it is hard to know in advance which reactions will be important. The objective is to choose some (very small) subset of the reactions to use in the mechanism so that the behavior of the reduced system is as close as possible to that of the original system, given a range of operating conditions.

If S is the matrix whose columns are the stoichiometric vectors, $S \in \Re^{n\times N}$, and $F \in \Re^n$ is the vector of nonlinear reaction terms, then the original system can be written more compactly as

$$y' = SF(y). \tag{3}$$

The reduced system is given by

$$z' = SDF(z), \tag{4}$$

where $D \in \Re^{N\times N}$ is a diagonal matrix whose diagonal elements d_i are either 1 or 0 (depending on whether or not reaction i is selected for the reduced mechanism). Then the problem of finding the reduced mechanism can be written as a constrained optimization

$$\begin{aligned} \min \quad & ||y - z|| \\ & \mathit{subject\ to} \\ & y' = SF(y), \quad y(0) = y_0 \\ & z' = SDF(z), \quad z(0) = y_0, \quad 0 \le t \le b & (5) \\ & \sum_{i=1}^{N} d_i = k, & (6) \end{aligned}$$

where the minimum is over $d_1, ..., d_N$, each d_i can take the value 0 or 1, and $k << N$. Currently in our approach the number k of reactions for the reduced mechanism is chosen by the user. If it is important to be sure that the reduced model is valid over a range of operating conditions, one should add additional constraints and the corresponding variables which are the differential equations for the original model and for the reduced order model, but with different initial conditions. By posing this problem directly as an optimization, there is also a natural measure for the error due to the reduced order model. We note that the norm should be weighted according to user tolerances for relative and absolute errors. In some situations it may be desirable to minimize over some other measure of the error; our methodology can easily accommodate such a modification.

3 Solving the integer programming problem

It would appear that solving the discrete optimization problem (6) directly could be very costly. Note that there are almost no mature methods for nonlinear integer programming problems without convex or polynomial properties, which is the case for (6). Also, note that it may not be necessary to find the absolute minimum; any reduced mechanism for which $||y - z||$ is small enough would meet our needs. To find a near-minimum, we consider solving the continuous optimization problem

$$\begin{aligned} \min \quad & ||y - z|| \\ & \text{subject} \quad \text{to} \\ & y' = SF(y), \quad y(0) = y_0 \\ & z' = SDF(z), \quad z(0) = y_0, \quad 0 \le t \le b, \\ & \sum_{i=1}^{N} d_i = k \end{aligned} \tag{7}$$

In some cases, the results of the continuous optimization problem (7) are of interest directly (for example, if the rate constants aren't known precisely). If it is the solution to the discrete problem (6) which is of interest, the continuous solution needs to be rounded to integer values.

A scheme which approximates the solution to a discrete problem via a continuous algorithm has been used successfully by Hendrickson and Leland [14] for example in multidimensional load balancing for parallel computation. Their general approach applied to our problem would be: first solve the continuous problem, then set those d_i which are greater than some threshold to 1 and the rest to 0, and possibly iterate with this as the initial guess. In our problem, we have to take a strict threshold because the problem is highly nonlinear and the objective is very sensitive to the parameter values. If we just round the results to 0 or 1 after some number of iterations, the integer solution may be much less satisfactory than the continuous solution. A rough round-off can result in an integer solution which is far away from a local optimum and may not be very useful for further iterations.

3.1 Reformulating the optimization problem

To ensure a small approximation error which is caused by rounding the continuous solutions to integers, some modifications to the optimization problem (7) need to be made. An approach we have found effective is to impose a nonlinear constraint on the original optimization problem. A penalty function method as described in [3] can be used but in practice we found the sequential quadratic programming(SQP) method of SNOPT [11] is more efficient when the nonlinear equality constraint is relaxed, i.e. replaced by an inequality constraint. In this paper, we give the numerical results obtained using the SQP method with the inequality constraint.

The SQP methods are a class of optimization methods that solve a quadratic programming subproblem at each iteration. Each QP subproblem minimizes a quadratic model of a certain modified Lagrangian function subject to linearized constraints. A merit function is used to select the best step size along each search direction. For an overview of SQP methods, see for example [7].

Using the SQP method, the optimization problem is formulated by

$$\begin{array}{ll} \min & ||y-z|| \\ & \text{subject} \quad \text{to} \\ & y' = SF(y), \quad y(0)=y_0 \\ & z' = SDF(z), \quad z(0)=y_0, \quad 0 \le t \le b, \\ & k_1 \le \sum_{i=1}^{N} d_i \le k_2, \\ & g(d_1,\cdots,d_N) \le r \end{array} \tag{8}$$

where $g(d_1,\cdots,d_N)$ is a nonlinear function which, when equal to 0, forces the d_i to take integer values. In (8), r is a positive number which acts as the relaxation of the nonlinear constraint and k_1, k_2 are two integers which are used to relax the linear constraint because only approximate solutions are needed.

Different kinds of nonlinear constraints can be used. The one we are currently using is from [8]

$$g = \sum_{i=1}^{N} (d_i - d_i^2)^{\beta} = 0, \tag{9}$$

where $\beta \ge 2$ is some parameter which controls the shape of the normalized, symmetrical Beta-function integrand. The gradients of the constraint are zero at integer points $d_i = 0$ or $d_i = 1$ for $i = 1,\cdots,n$. In our numerical experiments, β is taken to be 2.

3.2 Choosing the initial values

The continuous optimization code we are using can find only local optimal solutions for nonlinear programming problems. The chances of finding a global optimum are usually increased by choosing a starting point that is “sufficiently close” [11]. There are several ways to choose the initial guess. One way is to utilize chemical insight to guess a group of important reactions and set their corresponding d_i to 1 and the rest to 0. Another way is to use the greedy method to find an initial guess.

In the greedy method, the reactions are deleted from the original model one by one; each time, we drop the reaction which causes the smallest error between the original model and the current reduced model, under the given norm. Then all the reactions are ranked according to the order that they are deleted from the model. The initial guess is obtained by retaining the set of the most important reactions under the greedy criterion. The number of these reactions can be equal to the number of reactions we want to keep. The greedy method can in fact result in very good initial guesses, as we have observed in our preliminary experiments. The problem with this approach is that when we are dealing with very large reaction models, the cost of finding a greedy guess can be very high; it is of order $O(N^2)$.

Instead of using the greedy method, we can just compute the error caused by deleting a single reaction from the original model and then order all the reactions according to their corresponding errors, with the one that causes the smallest error considered to be the most unimportant reaction. If only a small number of reactions are to be deleted from the model, this method can be used to generate the initial guess. However, when a large number of reactions are to be deleted from the model, the initial guess generated by this method is not reliable. On the other hand, this method can be used to identify the most important reactions. Using this method, we pre-select those reactions whose absence will cause extremely large errors. Pre-selecting the most important reactions can avoid some difficulties we will explain in detail in Section 6. Optimization is then done over the remaining reactions. Similarly, those reactions that cause extremely small errors can be pre-deleted, which works well according to our numerical tests. This not only reduces the number of variables in the optimization problem but also makes the optimization problem easier to solve since it eliminates some bad near-integer points in the search region where no reaction actually happens and the errors are very large but the gradients of the objective are very small, though they are not necessarily local minimum or maximum points. This can be observed from the formulation of the objective, when some d_i’s are at 0 and many species have near-zero concentration. A post-recovery process described later can be used to recover the reactions that have been pre-deleted but can actually reduce the error significantly.

The simplest way to generate an initial guess is to set all the parameters to 1. This can be done when the model consists of a large number of reactions and we need to reduce it to a relatively small size. In this case, the two methods mentioned before are not appropriate and if we don’t have any chemical insight of the model, we have no other choice. Starting from all parameters equal to 1 is in fact a good choice in some situations as we will see later.

3.3 One-step or multi-step optimization with sensitivity parameter reducing

Using the initial values obtained above, with some reactions having already been pre-selected or pre-deleted, we can let the optimizer reduce the number of remaining reactions to the number we need in one step. Initially, the bounds on all the parameters are set to 0 and 1, i.e., all the parameters are sensitivity variables. Since the sensitivity analysis is expensive and for a large model, the number of sensitivity variables can be very large, we adopt a sensitivity variable reducing approach during the optimization process.

The approach works as follows. At the beginning of the optimization, every parameter is considered as a sensitivity variable. After a sufficient number of iterations of the optimization process, some of these parameters will be near 0 and remain small in the later iterations. We make an assumption that these parameters won't increase much and set both their lower and upper bounds to 0. A strict threshold must be taken to avoid deleting a reaction too early. The other parameters are set to 1 or take the previous value, and the optimization process is restarted. At this time, the parameters which are set to 0 will not be considered as sensitivity variables anymore. In this way, the number of sensitivity variables is monotonically decreasing and the optimization process is less expensive in later iterations. Since in a model, some reactions are much less important compared to others, they can be picked out first in a relatively small number of iterations by the optimizer, though each iteration is expensive. As these reactions are deleted, the optimizer can concentrate on those reactions that are similar to each other in importance. Thus, each subsequent iteration of the optimizer will be less expensive and the number of iterations can be increased to allow better resolution.

The one-step optimization approach can be used if the number of reactions in the original model and the required number of reactions of the reduced model do not differ too much. In this case, since the initial guess with all the parameters set to 1 is an optimal solution for the problem of reducing 0 reactions, it will be easier for the optimizer to find a new optimal solution for the problem of reducing M reactions with $M << N$ [23]. In this paper, we tested only the one-step approach since the models we used are not very large, i.e., not more than 200 reactions.

In case the number of reactions of the original model N is very large and also the number M of reactions to be deleted is close to N, we can take a multi-step optimization approach to help the optimizer converge to an optimal solution. The approach works as a series of one-step optimizations with a relatively small M_i in each step. Each step takes the result of the previous one as initial guess and sets the lower and upper bounds to 0 for those parameters deleted in the previous steps, similar to the one-step approach. Though this scheme may take more iterations than the one-step approach, we hope it can give a better solution.

For systems which have an even larger number of reactions, grouping of the reactions can help. The reactions in the original mechanism can be divided randomly into a number of groups, each containing several reactions, to reduce the number of sensitivity parameters. The optimization process described before can then be applied to these groups to get a reduced number of groups. The number of the reduced groups should usually be greater than the number of reactions we want to keep in the reduced mechanism, in order to allow each reaction in the final reduced mechanism the chance to be kept eventually. The implicit assumption of the grouping approach is that the reactions in the original mechanism differ greatly in their importance. In other words a group of reactions that are not important will not have as much effect on the mechanism as a single reaction which is important. Otherwise, a group of secondary reactions may be considered as more important than a group which contains only one important reaction. Thus the important reactions may be lost during the process and we may eventually arrive at a set of secondary important reactions. However our assumption is usually true when the number of reactions in the original mechanism is very large and only a small fraction of reactions can be kept. This grouping process can repeated several times to reduce the original mechanism to a desired size.

The grouping approach can reduce the computational work drastically. This can be seen from the following example. Suppose we want to reduce a full mechanism of $M * 2^N$ reactions to a mechanism of $M/2$ reactions. At the fist step, we divide these reactions into M groups, each containing 2^n reactions, and try to select $M/2$ groups to keep. Let's suppose the number of species to be K, then the size of the sensitivity analysis problem to be solved is about KM. At the second step, the number of reactions remaining will be $M * 2^{N-1}$. We again divide them into M groups and try to keep $M/2$ groups. The group size is half as large as before but the size of the sensitivity problem is still $K * M$. We can repeat this process N times to reduce the number of reactions to $M/2$. If we suppose that at each step, the optimizer needs the same number of integrations of the ODE system, say L times, and the time for each integration is proportional to the size of the system, then the time for the whole process is about $LKMN$. If no grouping is used, then the time will be about $LKM * 2^N$. Even though the actual time for one integration of the sensitivity system will not increase linearly with the number of sensitivity equations, the difference between these two approaches can still differ dramatically. Another advantage of grouping is that the time spent on each step is much less than if no grouping is used, even when N is not very large. This makes it easier to monitor the performance of the optimizer.

4 Implementation and numerical results

In our implementation, the continuous optimization is done via DASOPT, a code for parameter estimation and optimal control of differential-algebraic systems which is currently under development [22]. This code solves the class of problems

$$find \quad u(t) \; and \; x(t) \; for \; t_0 \leq t \leq t_f \tag{10}$$

$$to\, minimize \quad J \;=\; \int_{t_0}^{t_f} L(x(t), u(t), t)dt \;+\; V(x(t_f)) \tag{11}$$

$$subject\; to \;\; f(t, x(t), x'(t), u(t)) \;=\; 0 \tag{12}$$

$$g(t, x(t), u(t)) \;\geq\; 0. \tag{13}$$

In the above, x is the state time history vector, u is the control time history vector, t_0 is the initial time, and t_f is the final time. The DAE (12) defines the dynamics of the system and the inequalities (13) are additional constraints.

The optimal control problem is solved using nonlinear programming (NP) techniques. The problem is first discretized along the time domain, resulting in a discrete-time optimal control problem with finitely many unknown variables, or equivalently, a constrained NP problem. The DAEs are solved via DASPKSO [4, 18] over each subinterval. Continuity conditions between the subintervals are expressed as constraints in the optimization problem. The derivatives for the optimization are computed via the DAE sensitivity code DASPKSO [18]. Thus the sensitivity calculation is a part of this approach. However, there is an important difference between the proposed method and sensitivity analysis alone. During the optimization, the sensitivities for each iteration are computed by perturbing the rate constants around some value, determined by the optimization method, which could be closer to zero than to the nominal value of the rate constant. Thus the information is available to decide more reliably whether a reaction could be deleted from the mechanism. The resulting optimization problem is solved via SNOPT [11]. This software can solve optimization problems with very large, sparse Hessian matrices. SNOPT uses the sequential quadratic programming (SQP) method to update the Quasi-Newton approximation of the reduced Hessian, which greatly reduces the matrix size, especially in optimal control problems that preserve many active constraints at each iteration.

In the present formulation of our problem, the control parameters are constants in the time interval under consideration, and (12) is an ODE. The vector field of the ODE is formed by using Chemkin [15]. An additional equation which finds the norm for the objective function is added to the system formed by Chemkin

$$u' = \sum_{k=1}^{K} (y_k - z_k)^2. \tag{14}$$

The reduced model depends not only on the norm but also on the initial concentrations of the species and the initial temperature and pressure. Since we use the mass fractions of the chemical species, y_i is between 0 and 1. As the number of species in a chemical mechanism increases, the mass fractions of most species are very small while temperature is usually very high. In our test mechanisms, temperatures are of the scale 10^3. To balance the effects of the species and temperature in the objective function, we scale up the mass fractions of the species in the objective function. In the numerical result of this report, the scale-up for the species is taken to be 10^3, which makes the total effect of the species comparable to that of the temperature.

The error of the reduced model is compared to the norm of the error which results when all the reactions are deleted. The time interval is important in our problem. Since chemical mechanisms are often highly stiff, they can reach a steady state very fast. Taking a long time interval will give slow reactions more importance. A short time interval will catch the fast reactions, i.e., catch the stiffness. In this preliminary report, we have taken short time intervals. In this situation, the error will usually be small because it's an integral over the time interval taken. We also scale up the norm according to the integration interval. This results in a better scaling for the objective function and its gradients; thus the optimizer can perform better. In this report, the scale-up for the norm is taken as the reciprocal of the time interval.

The residual functions for the sensitivity equations, and the Jacobian matrix required by DASPKSO are supplied by ADIFOR [2], an automatic differentiation tool.

Numerical results of the SQP method for three chemical mechanisms are given below. In our computations, the parameters are associated with the reactions in the input file for Chemkin. If the original file contains reversible reactions, then each parameter is associated with a reversible reaction. If forward and backward reactions are input separately, then each forward and and backward reaction is associated with a parameter. A detailed description of the corresponding chemical mechanisms are given in the Appendix, as well as the reduced mechanisms which we obtained.

4.1 Example 1: 6-reaction ozone mechanism

Using the methods proposed in this report, we reduced this very small mechanism to 3 reactions in the time interval $[0, 1.0]$. By observing the iteration process of the optimizer, we find that reactions 1 and 3 are always picked by the optimizer but it encounters difficulty when deciding which of the other ones it should pick: 4 or 6. This suggests that reactions 4 and 6 are similar in their effect to the original system. Picking either one of them results in similar total errors. We reduced further the system to 2 reactions. This time the optimizer gave the answer as 1 and 3, which we can almost guess from the previous process. The trajectories of temperature and of the species with a significant amount of mass fraction are shown in Figures 1-3. These results are very similar to that of 3 reactions which are not presented here. We can see from these figures that there is a time delay in the ignition for the reduced model.

If we pre-select reactions 1 and 3 and let the optimizer pick the third important reaction, it will easily find 2. We conjecture that this kind of problem may due to the nonlinearity of the system.

Reactions 1-3 yields a very good reduced model: there is almost no error, as shown in Figures 4-6. Reaction 2 seems to be controlling the ignition time. This suggests that a post-recovery process may be necessary to get the secondary important reactions like 2 after the most important reactions (1 and 3) are found. This can be accomplished by several approaches which we will show in Section 6.

Since we are using the scaled L_2 norm of the temperature and species mass fractions, the optimizer captures only the perturbations of species with significant mass fraction. To see the perturbations of species with very small mass fraction, we need to weight their corresponding terms in the L_2 norm, which can be done if one is interested in the change of some specific species. The scale-up can be determined based on the concentration of the species of interest. We just need to make the effect of these species in the objective comparable to that of temperature. For example, if the concentration of a species is around 0.01 during the time interval under consideration, a scale-up of 10^5 is appropriate.

4.2 Example 2: 20-reaction mechanism

This mechanism is similar to the example mechanism in [15] except that the element N and all reactions in which it is involved are not included here. It describes constant pressure combustion for a hydrogen-oxygen mixture. One reduced model is given by the first six elementary reactions of the original mechanism. The solution of this reduced model matches the original model well on the time interval $[0.0, 10^{-2}]$ on which the optimization is done. Figures 7-10 show temperature and some of the species which change significantly in the time interval considered. As the figures manifest, after a short ignition phase, the system reaches steady state and the mass fractions of the species do not change much.

4.3 Example 3: GRI Mechanism

GRI-Mech 1.2 is one of the optimized detailed chemical reaction mechanisms capable of the best representation of natural gas flames and ignition. Most of the reactions listed in this mechanism have been studied one way or another in the laboratory. Thus the rate constant parameters mostly have more or less direct measurements behind them. The original GRI mechanism 1.2 [10] contains 177 reversible reactions. We reduced this mechanism to 78, 42 and 32 reactions on the time interval $[0, 1]$. The 78-reaction reduced model is obtained by dividing the 177 reactions in the original model into 59 groups and then selecting 26 from them. It models the steady state of the system very well, as shown in Figures 11-15.

The groups are actually formed as follows. First a group size is chosen according to the number of reactions such that the number of groups is not too large, say, less than 100 but still larger than the number of reactions we want to keep in the final reduced mechanism. For this example, we took the group size to be 3, resulting in 59 groups. The number of groups is taken as the step size when forming the groups to ensure randomness. Actually, this may not be necessary since the possibility that several most important reactions are in the same group won't cause any difficulty: this just reduces the number of groups that can contain those most important reactions. In this problem, reactions 1, 60 and 119 form the first group, reactions 2, 61, 120 form the second group and so on. Since in the general case, we can not guarantee that the number of reactions can be divided evenly by the group size, the last group will consist of the last several reactions in the original system.

A reduced mechanism of 42 reactions was obtained by pre-selecting the 17 most important reactions using the scanning method described earlier and optimizing over the remaining reactions. The results are satisfactory, as shown in Figures 16-20, though the steady state of the original mechanism and that of the reduced mechanism are slightly different.

The smallest reduced mechanism we obtained so far without using the post recovery process is a 32-reaction mechanism. This mechanism models the ignition time and the steady state of the original mechanism well but it does not model the shape of the trajectories very well, as shown in Figures 21-25. Numerical experiments show that it is difficult to reduce the number of reactions to below 30 without out using the post recovery process if the steady state of the original mechanism is to be modeled accurately. A smaller reduced model with 26 reactions is obtained using the combination of discrete approach on species and the post recovery process on reactions which we will show in Section 6. Some small reduced models are listed in the Appendix B.

5 Reducing the number of species

In many problems, reduction of the number of species is also important. Reduction of the number of species can reduce the number of ODEs to be solved and save computation time.

As we are now reducing reactions directly, the species are "deleted" when all of the reactions in which they take part are deleted. Here, the deletion of a species just means that its concentration won't change in the given time interval. It does not mean that those species are no longer taking part in the reactions, since some of the reactions involving those species not deleted are enhanced by them. To actually delete a species, we need to not only delete the reactions it takes part in but also its effect to those reactions enhanced by it. This makes the problem more complex for the optimization, i.e., it introduces more nonlinearity to the optimization problem as we can see later. So far, we have considered the deletion of a species by fixing its concentration and deleting all the reactions it takes part in.

One way to do this is to adapt our general approach to reduce the number of species directly, i.e., to associate with each species a parameter and then do the optimization. Because the number of species is much smaller than the number of reactions, the sensitivity analysis for the parameters is less expensive. The optimization problem can be formulated as:

$$\begin{aligned} \min \quad & \|y - z\| \\ & \text{subject to} \\ & y' = SF(y), \quad y(0) = y_0 \\ & z' = SDF(z), \quad z(0) = y_0, \quad 0 \le t \le b, \\ & k_1 \le \sum_{i=1}^{N} e_i \le k_2, \\ & g(e_1, \cdots, e_N) \le r \end{aligned} \tag{15}$$

where e_i's are parameters associated with species and $g(e_1, \cdots, e_N)$ is a nonlinear function which, when equal to 0, forces the e_i to take integer values. The difference is that now the elements of the diagonal matrix D are computed by

$$d_i = \Pi_{j \in R_i} e_j \tag{16}$$

where R_i is the set of species which take part in reaction i. Thus when $e_j = 0$ for some $j \in R_i$, the reaction i is in fact deleted because $d_i = 0$. We see that this optimization problem is well defined when all the parameters take values of 0 or 1. Unfortunately, this formula, when e_i's are allowed to take continuous values, is highly nonlinear. The rounding process is much more troublesome than in reducing the number of reactions. Numerical experiments demonstrate this. Even though the continuous problem gives solutions where the e_i's are very close to 0 or 1 and the objective is very small, the rounding process can destroy the solution, even when very strict thresholds are used. A better formulation of the problem needs to be found.

Since as we mentioned before, the number of species is usually much less than the number of reactions, scanning on the species is much less expensive than scanning on the reactions. For example, the GRI model contains 177 reactions but only 32 species. For larger mechanisms, the difference is even more significant. The scanning on the species works as follows. We simply pick a species and delete all the reactions that it is involved in as a reactant or product, to arrive at a reduced mechanism. The solution of this mechanism is compared with that of the original mechanism to obtain the error caused by the “deletion” of this species. Repeating this process on all the species in the mechanism completes one scanning on the species. The result of the scanning on the species is listed in Figure 26, where the species are numbered the same way as in Figure 36. For the detailed GRI mechanism, please refer to [10].

In this table, the temperatures are that of the reduced models at the end of the time interval when only the corresponding species are deleted from the model. The

'Reactions Remaining' column gives the sizes of the reduced models when only the corresponding species is "deleted" from the model. Since the starting temperature is 1000, we can see from the list that deletion of a single species from the set of {4-7, 13-18, 20} will let nothing happen physically since the temperature is not increased and also the error is very large. Deleting more of them gives similar results. So we expect that these 11 species will have to be kept. Species 1-3, which cause the temperature of the reduced model to be higher than that of the original model, also cause the next largest error. Adding them into this set makes the steady state of the reduced system model the original system very well but the ignition time is not modeled very well, as Figure 27 shows. Note that keeping a species does not mean to keep all the reactions in which it is involved, though deleting a species does mean to delete all the reactions it takes part in.

An interesting result is that when species 25-27 are also included, the reduced model has almost no error. This reduced model has only 67 reactions. The figures for this reduced model are not given since they are the same as the original model.

This result of the scanning on the species suggests that scanning on species may be a better choice than scanning on the reactions. A modified approach can work like this: first the species are scanned and a reduced model which causes almost no error is found. This is much less expensive than scanning the reactions first. Then the reduced model is scanned a second time on reactions to produce a model which causes almost no error. This reduced model is then fed to the optimizer for further reduction. The work of the optimization is thus reduced considerably and also it can work more efficiently if further reduction is possible. Figure 28 shows the temperature of a 38-reaction reduced model which is obtained from scanning on the reactions of the 67-reaction model and no optimization. The reduced model results in almost no error and leaves very little space for the optimizer for further reduction, as our numerical experiments demonstrate. Figures for species are not given here because they are also the same as that of the original mechanism. The 16-species and 38 reaction model is listed in the Appendix. Note that species are not actually deleted from the model; instead, their concentrations are fixed. So they still appear in the species list of the input file to Chemkin.

6 Post recovery process and pre-selection of important reactions

Even though we are taking strict thresholds, the step that rounds to an integer solution can still cause problems. A post recovery process is needed to improve the result as shown in Example 1. Our numerical experiments show that in some extreme cases, a threshold as small as 0.001 can fail to give a satisfactory integer solution. These failures are due to the high degree of nonlinearity of the optimization problem and the huge difference in the reaction rate constants. The reason for the first difficulty is obvious. The reason for the second difficulty can be illustrated by the following example.

Consider the following scalar ODE

$$y' = -(\lambda_1 + \lambda_2)y, \quad y(0) = 1.0$$

where $\lambda_1 >> \lambda_2 > 0$. We hope to use the optimization method to select one term which can approximate the original system best. The parameterized system is

$$z' = -(d_1\lambda_1 + d_2\lambda_2)z.$$

Reducing the system to one term requires solving the optimization problem with constraint $d_1 + d_2 = 1$. The correct integer solution should be $d_1 = 1, d_2 = 0$.

For simplicity, we take the error norm as

$$\int_0^{t_1} (z(t) - y(t))dt.$$

When $(d_1\lambda_1 + d_2\lambda_2)t_1$ and $(\lambda_1 + \lambda_2)t_1$ are large enough, exponential terms in the error can be neglected and the error can be approximated by

$$1/(d_1\lambda_1 + d_2\lambda_2) - 1/(\lambda_1 + \lambda_2).$$

The derivatives of the error norm with respect to d_1 and d_2 are

$$-\lambda_1(d_1\lambda_1 + d_2\lambda_2)^{-2} \quad \text{and} \quad -\lambda_2(d_1\lambda_1 + d_2\lambda_2)^{-2}.$$

When $d_1 << d_2 < 1$ but $d_1^2\lambda_1 >> 1$, the gradient to d_1 can be small and the optimizer may prematurely declare the current d_1, d_2 to be the optimal solution when the optimality tolerance is not very strict, thus the rounding process gives a wrong answer as it takes $d_2 = 1, d_1 = 0$.

To solve this problem, a post recovery process is needed to improve the result. This can be done in several ways:

- use the optimization method to pick several more reactions
- perform a sensitivity analysis at 0 of the reactions rounded to 0 to find those reactions that have an extremely large negative derivative value
- use the greedy method to find the deleted reactions that improve the objective function most

The 3-reaction reduced model for Example 3 is obtained via the first approach. We have also used the second approach to obtain a 26-reaction reduced model for Example 3, which is reduced from the 17-species, 38-reaction reduced model in Section 5. We first try to reduce the 38-reaction model to 19 reactions. After a rounding process with threshold 0.03, an integer solution which keeps 19 reactions is obtained but it gives a poor objective. We then use sensitivity analysis to recover the 6 reactions which have the largest negative derivatives, to obtain this 26-reaction reduced model which is actually better than the larger models we obtained before. The results are shown in Figures 29-33.

Due to the very large scale difference in the reaction rate constants, some reactions are much more important than others. These most important reactions can be pre-included in the reduced model. This not only saves computation time but can also avoid some numerical difficulties. In fact, there are some small subsets of reactions of the original mechanism which allow no physical reactions to happen and can result in very large objective values. However, the gradients of the objective can be very small for these subsets of reactions. The reason is that these subsets of reactions lack more than one key reaction to allow the physical reaction to happen. So the objective is not sensitive to the perturbation in each single parameter. These subsets of reactions are bad local minimums and should be avoided. This is done by pre-selecting the most important reactions. Thus pre-selecting the most important reactions can help the convergence of the optimizer.

Some subsets of reactions that just lack one key reaction to allow the physical reaction to happen can be very sensisitive to small perturbations in species concentrations and reaction constants of the key reaction. The dynamical systems of these subsets of reactions can have very ill conditioned Jacobian matrices and more seriously, extremely large scale differences in the sensitivity variables. We have encountered examples with a difference in the scale of the sensitivity variables as large as 10^{-100} and 10^{+50}. Actually the sensitivity to the key reaction is extremely large, i.e., a very small perturbation of the reaction constant from 0 can let the physical reaction happen and thus reduce the error norm drastically. However, some other reactions may not be so important; a small perturbation to each one of these reaction constants from 0 will not cause the physical reaction to happen, and thus the sensitivity to these reaction constants are almost 0. As we have no prior knowledge of the scaling of the sensitivity variables, scaling can be a very serious problem without a technique to do automatic scaling. Pre-selecting the most important reactions can alleviate this difficulty.

7 Future work

Besides the problems we mentioned before, we plan to systematically test the algorithm proposed here and use the approach to reduce large chemical kinetics mechanisms.

An important issue in this model reduction problem is how to decide whether a given reduced mechanism is acceptable. In our scheme, this means finding an appropriate measure for the distance between the original and the reduced mechanism. This may differ depending on what the reduced mechanism is to be used for. Techniques for translating the requirements specified by the chemists to an appropriate measure will be needed. There are many situations where the L_2 norm does not appear to be an appropriate measure, and even in situations where it is a good measure, scaling of the variables is critical. In some problems, it is the "shape" of the solution that is important. For example, a small shift in the time axis may be acceptable in the reduced mechanism.

As the reduced mechanisms are obtained under some specific initial conditions of the system, another important question is what is the range of the initial conditions under which the reduced mechanism is a good model. This seems to be a very difficult problem.

Acknowledgment

We would like to thank Dr. Tony Dean and Dr. Bill Green of Exxon Research and Engineering Co. for bringing this problem to our attention, and for their interest, advice and support for this work. Thanks are also due to Prof. J. Ben Rosen for his encouragement and advice in the area of numerical methods for mixed integer nonlinear programming problems.

References

[1] D. L. Allara and D. Edelson, *A computational modeling study of the low-temperature pyrolysis of n-alkanes; mechanisms of propane, n-butane, and n-pentane pyrolyses*, Int. J. Chem. Kinet. 7, (1975), 479-507.

[2] C. Bischof, A. Carle, G. Corliss, A. Griewank and P. Hovland, *ADIFOR - Generating derivative codes from Fortran programs*, Scientific Programming 1 (1992), 11-29.

[3] M. Bazaraa and C. Shetty, Nonlinear Programming, Wiley, New York(1979).

[4] K.E. Brenan, S.L. Campbell and L.R. Petzold, Numerical Solution of Initial-value Problems in Differential-Algebraic Equations, Second Edition, SIAM, 1995.

[5] R.W. Carr, JR., D.G. *Peterson and F.K. Smith, Flash Photolysis of 1,3-Dichlorotetrafluoroacetone in the Presence of Oxygen, Kinetics and Mechanism of the Oxidation of the Chlorodifluoromethyl Radicals*, Journal of Physical Chemistry, Vol. 90(1986), 607.

[6] D. Edelson, *Computer simulation in chemical kinetics*, Science 214 (1981), 981-986.

[7] P.E. Gill, W. Murray, M.A. Saunders and M.H. Wright, *Model building and practical aspects of nonlinear programming*, Computational Mathematical Programming, Series F: Computer and Systems Science, Vol. 15, 1985.

[8] K.M. Gisvold and J. Moe, *A method for nonlinear mixed-integer programming and its application to design problems*, Journal of Engineering for Industry, 1972.

[9] O. Gautier and R.W. Carr, JR., *Variational Sensitivity Analysis of a Photochemical Smog Mechanism*, International Journal of Chemical Kinetics, Vol. 17(1985), 1347-1364.

[10] M. Frenklach, H. Wang, C.-L. Yu, M. Goldenberg, C.T. Bowman, R.K. Hanson, D.F. Davidson, E.J. Chang, G.P. Smith, D.M. Golden, W.C. Gardiner and V. Lissianski, *http://www.me.berkeley.edu/gri_mech/*; and Gas Research Institute Topical Report: M. Frenklach, H. Wang, M. Goldenberg, G.P. Smith, D.M. Golden, C.T. Bowman, R.K. Hanson, W.C. Gardiner and V. Lissianski, *GRI-Mech—An Optimized Detailed Chemical Reaction Mechanism for Methane Combustion,* Report No. GRI-95/0058, November 1, 1995.

[11] P. E. Gill, W. Murray and M. A. Saunders, *Large-scale SQP methods and their application in trajectory optimization*, International Series of Numerical Mathematics, Vol. 115, Birkhauser 1994, 29-42.

[12] E. Grimme, D. Sorensen and P. VanDooren, *Stable partial realizations via an implicitly restarted Lanczos method*, preprint, 1994.

[13] E. Grimme, *An implicitly restarted Lanczos method for the model reduction of stable large-scale systems*, Thesis, University of Illinois at Urbana-Champaign Dept. of Electrical Engineering, 1994.

[14] B. Hendrickson and R. Leland, *Multidimensional spectral load balancing*, Proc. 6th SIAM Conf. on Parallel Processing for Scientific Computing, ed. R. Sincovec, D. Keyes, M. Leuze, L. Petzold and D. Reed, 1993.

[15] R.J. Kee, F.M. Rupley and J.A. Miller, *Chemkin-II: A Fortran Chemical Kinetics Package for the Analysis of Gas Phase Chemical Kinetics*, Sandia Report SAND89-8009B, UC-706, 1989.

[16] S. H. Lam, *Using CSP to understand complex chemical kinetics*, Combust. Sci. and Tech. 89 (1993), 375-404.

[17] S. H. Lam and D. A. Goussis, *Conventional asymptotics and computational singular perturbation for simplified kinetics modelling*, reprint, 1993.

[18] T. Maly and L.R. Petzold, *Numerical methods for sensitivity analysis of differential-algebraic systems*, Applied Numerical Mathematics 20(1996), 57-79.

[19] U. Maas and S. B. Pope, *Simplifying chemical kinetics: Intrinsic low-dimensional manifolds in composition space*, Combustion and Flame 88 (1992), 239-264.

[20] N. Peters, *Numerical and asymptotic analysis of systematically reduced reaction schemes for hydrocarbon flames*, Lecture Notes in Physics 241, 90-109, Springer Verlag, Berlin(1985).

[21] N. Peters, *Reducing mechanisms, Reduced Kinetic Mechanisms and Asymptotic Approximations for Methane-Air Flames*, Springer-Verlag, Berlin-Heidelberg(1991).

[22] L. Petzold, J.B. Rosen, P.E. Gill, L.O. Jay and K. Park, *Numerical Optimal Control of Parabolic PDEs Using DASOPT*, Proc. IMA Workshop on Large-Scale Optimization, 1996.

[23] J.B. Rosen, Personal communication.

[24] C. Seigneur, G. Stephanopoulos and R.W. Carr, JR., *Dynamic Sensitivity analysis of Chemical Reaction Systems*, Chemical Engineering Science, Vol. 17, No. 6(1982), 845-853.

[25] S. Vajda, P. Valko and T. Turanyi, *Principal component analysis of kinetic models*, Int. J. of Chemical Kinetics 17 (1985), 55-81.

[26] F. A. Williams, *Combustion Theory, The Fundamental Theory of Chemically Reacting Systems*, 2nd Edition, Benjamin Cummings Publ. Co., Menlo Park, CA., 1985.

Appendix A: Figures for Numerical Experiments

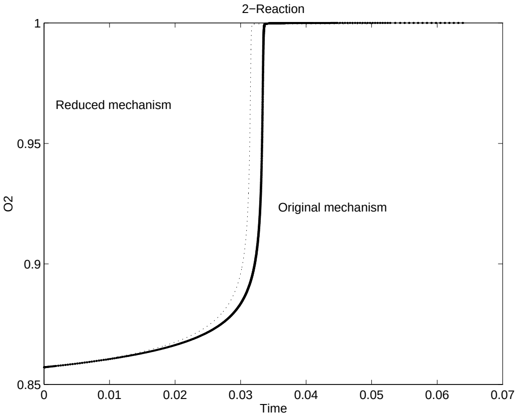


Fig 1. 2-Reaction Reduced Mechanism for Example 1

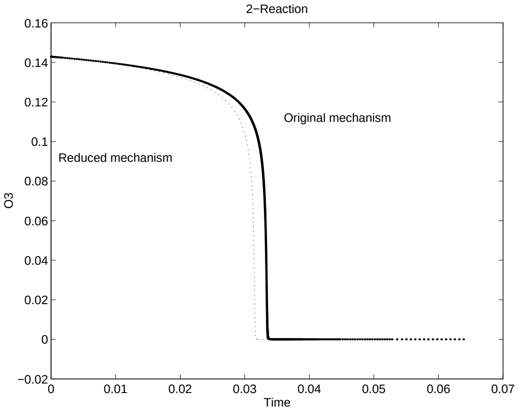


Fig 2. 2-Reaction Reduced Mechanism for Example 1

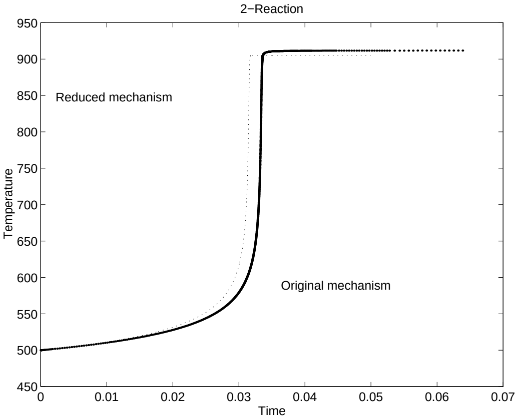


Fig 3. 2-Reaction Reduced Mechanism for Example 1

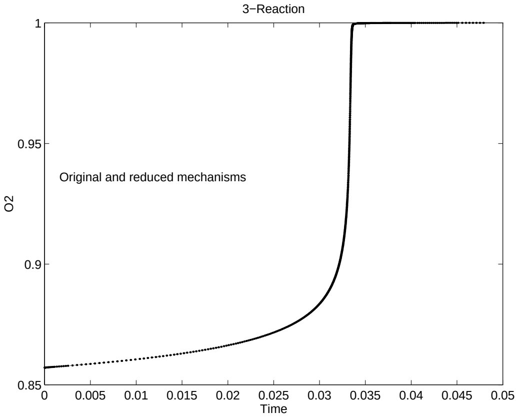


Fig 4. 3-Reaction Reduced Mechanism for Example 1

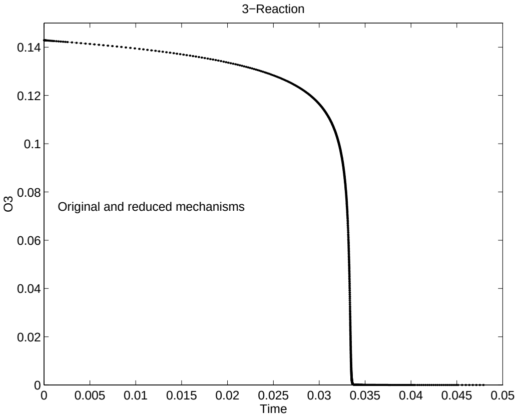


Fig 5. 3-Reaction Reduced Mechanism for Example 1

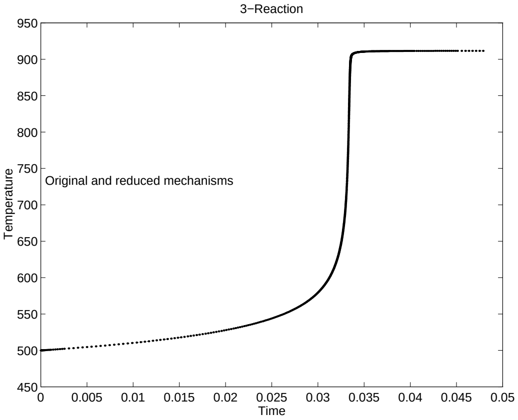


Fig 6. 3-Reaction Reduced Mechanism for Example 1

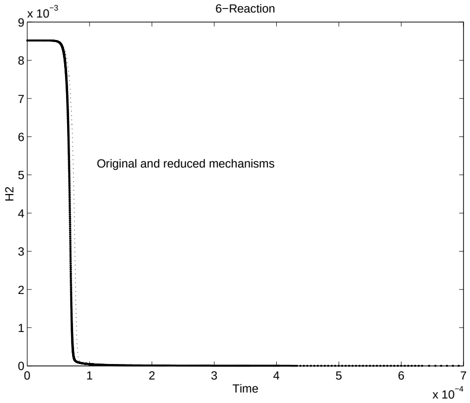


Fig 7. 6-Reaction Reduced Mechanism for Example 2

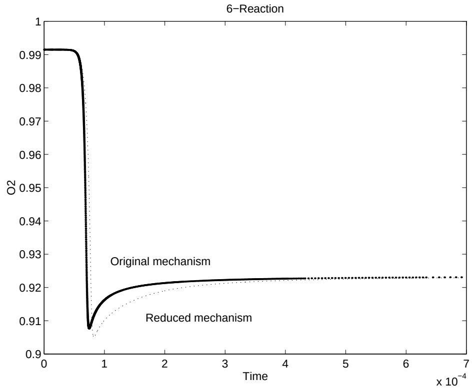


Fig 8. 6-Reaction Reduced Mechanism for Example 2

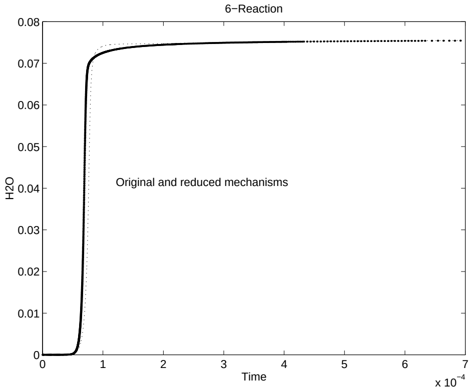


Fig 9. 6-Reaction Reduced Mechanism for Example 2

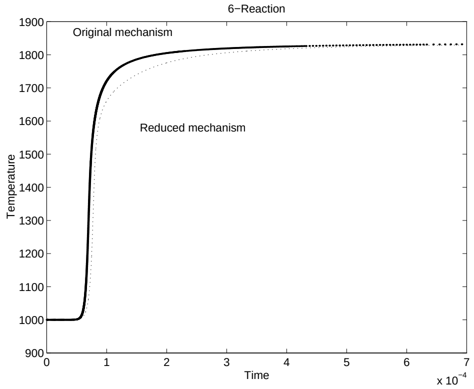


Fig 10. 6-Reaction Reduced Mechanism for Example 2

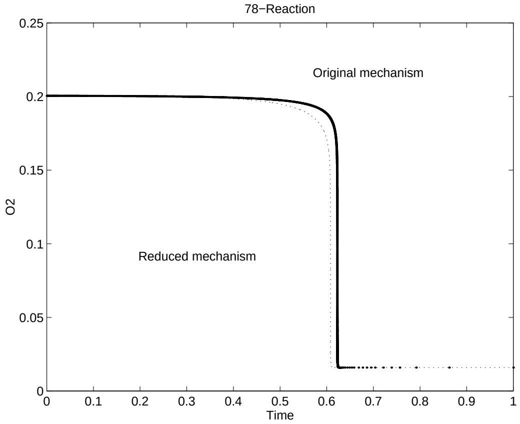


Fig 11. 78-Reaction Reduced Mechanism for Example 3

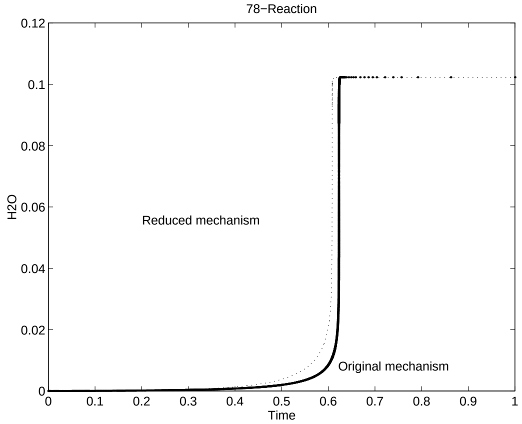


Fig 12. 78-Reaction Reduced Mechanism for Example 3

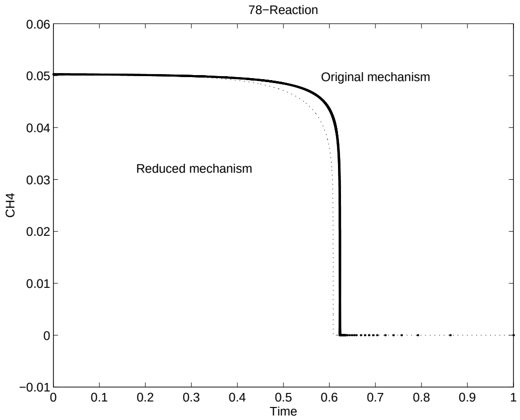


Fig 13. 78-Reaction Reduced Mechanism for Example 3

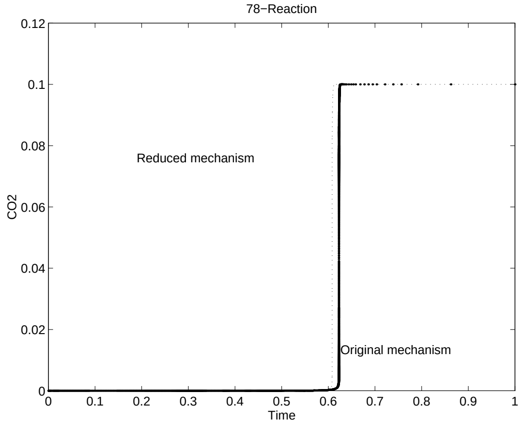


Fig 14. 78-Reaction Reduced Mechanism for Example 3

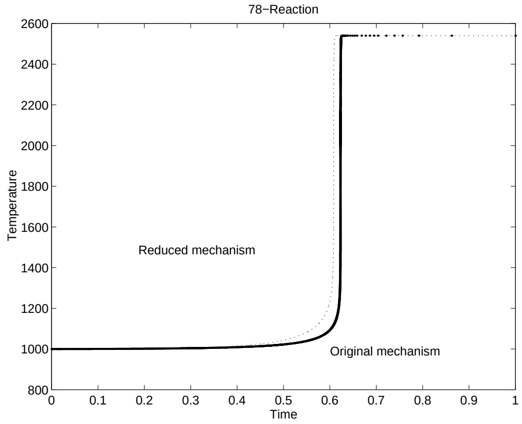


Fig 15. 78-Reaction Reduced Mechanism for Example 3

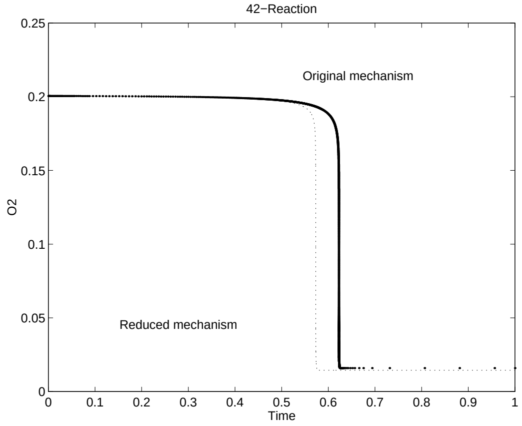


Fig 16. 42-Reaction Reduced Mechanism for Example 3

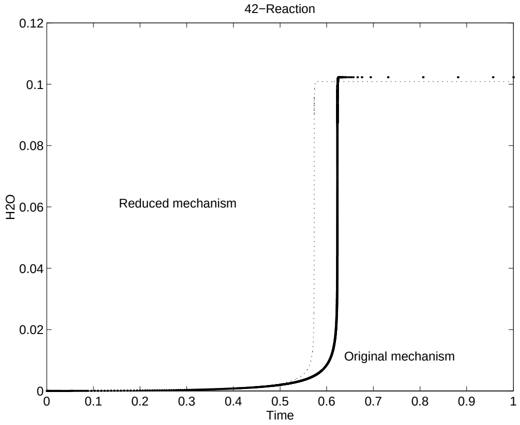


Fig 17. 42-Reaction Reduced Mechanism for Example 3

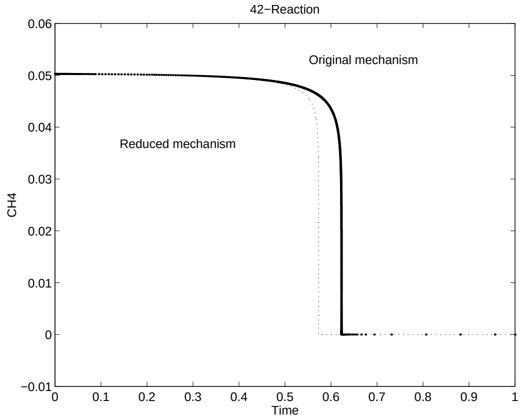


Fig 18. 42-Reaction Reduced Mechanism for Example 3

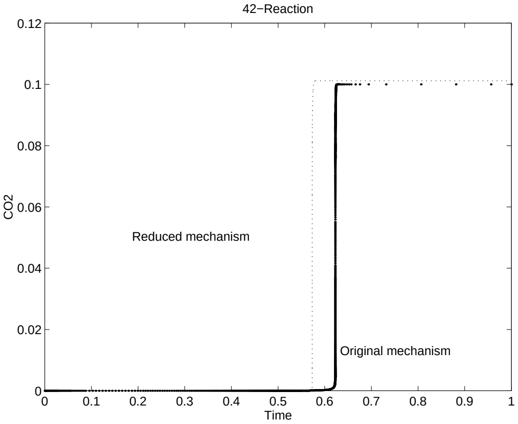


Fig 19. 42-Reaction Reduced Mechanism for Example 3

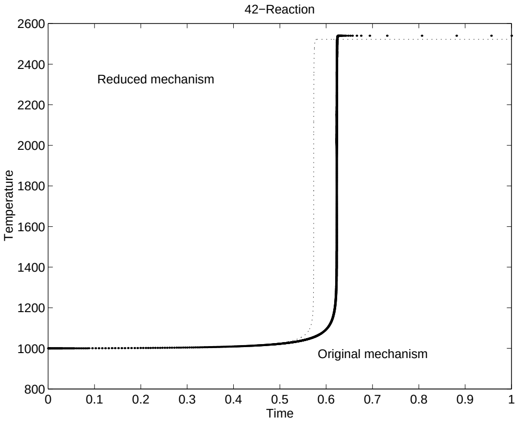


Fig 20. 42-Reaction Reduced Mechanism for Example 3

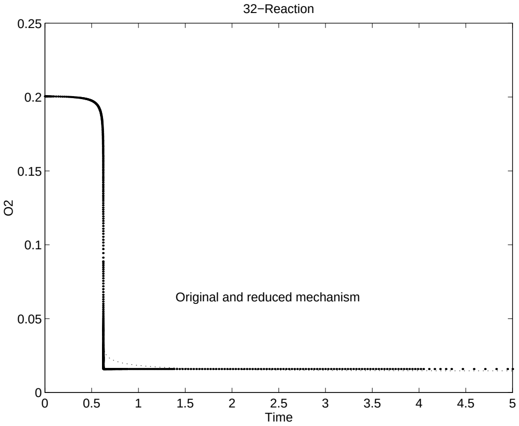


Fig 21. 32-Reaction Reduced Mechanism for Example 3

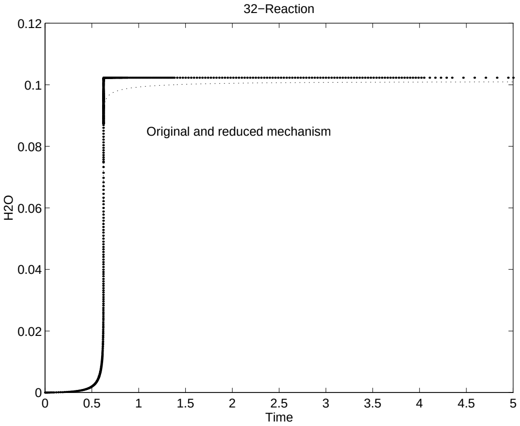


Fig 22. 32-Reaction Reduced Mechanism for Example 3

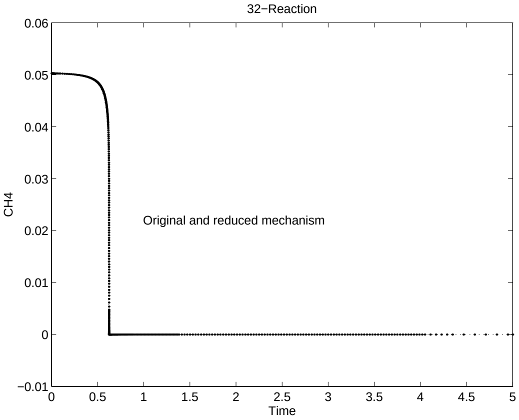


Fig 23. 32-Reaction Reduced Mechanism for Example 3

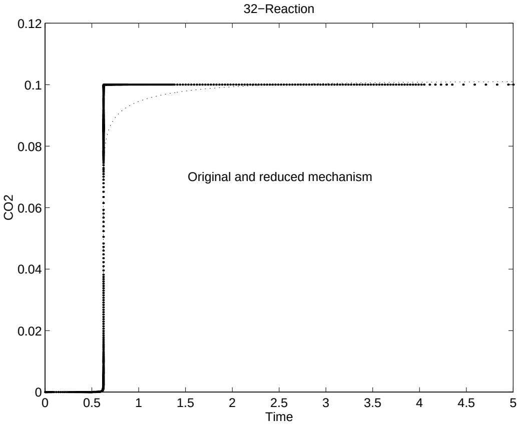


Fig 24. 32-Reaction Reduced Mechanism for Example 3

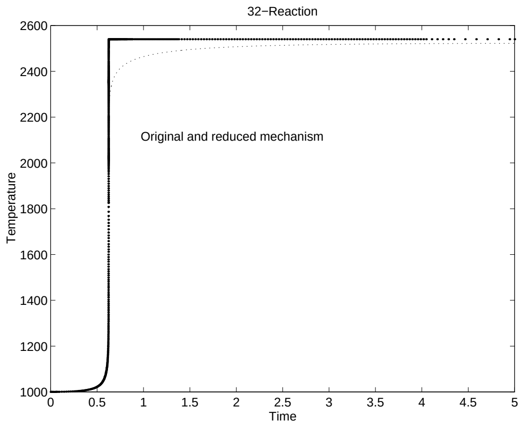


Fig 25. 32-Reaction Reduced Mechanism for Example 3

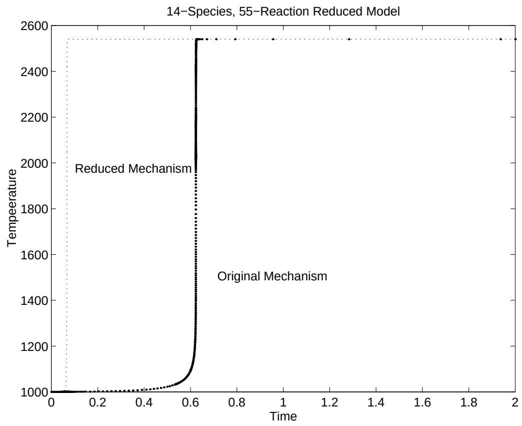


Fig 27. Reduced Model of 14 Species and 55 Reactions for Example 3

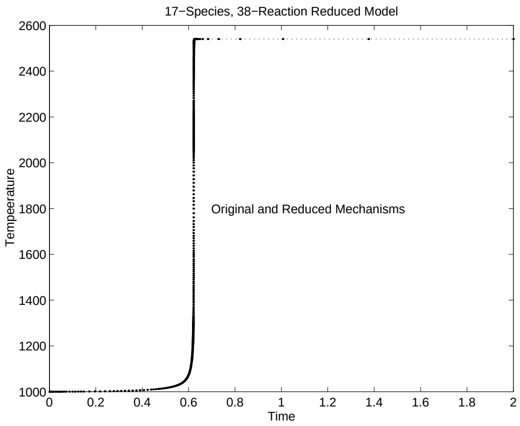


Fig 28. Reduced Model of 17 Species and 38 Reactions for Example 3

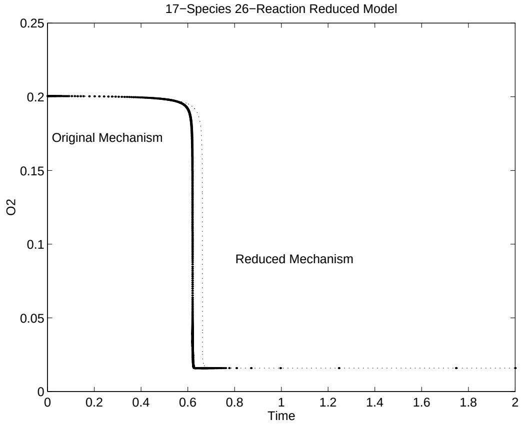


Fig 29. Reduced Model of 17 Species and 26 Reactions for Example 3

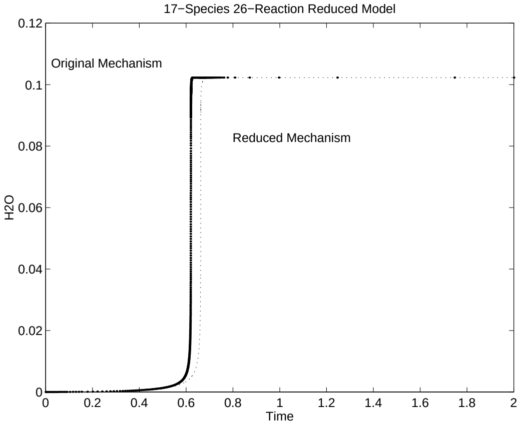
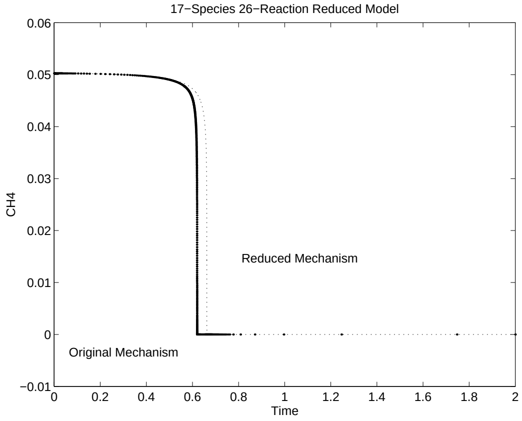


Fig 30. Reduced Model of 17 Species and 26 Reactions for Example 3



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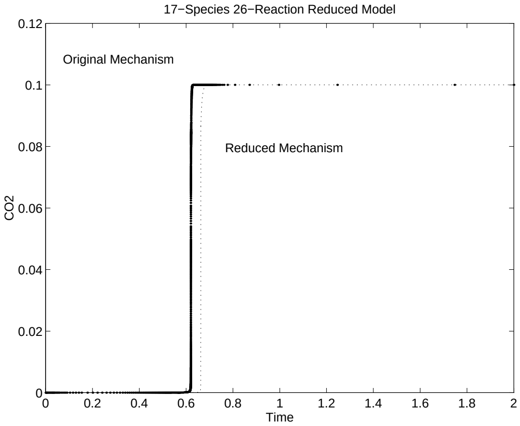


Fig 32. Reduced Model of 17 Species and 26 Reactions for Example 3

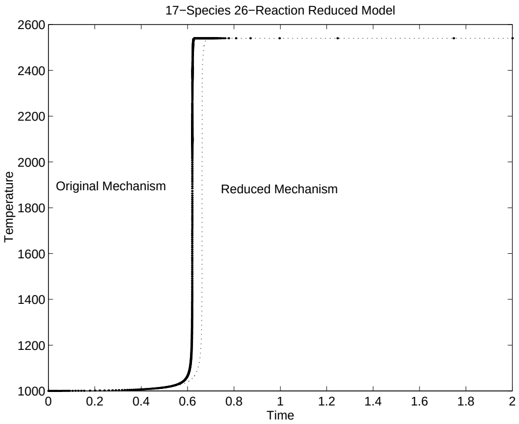


Fig 33. Reduced Model of 17 Species and 26 Reactions for Example 3

Species No.	Temperature	Error	Reactions Remaining
1	2563.846	327129.140	147
2	2578.462	145312.066	93
3	2548.987	566965.623	140
4	999.9999	1673740.07	148
5	1000.195	1673394.24	119
6	1000.299	1673278.93	149
7	1040.797	1642273.18	150
8	2540.034	5276.86882	167
9	2540.034	0.00010808	172
10	2540.034	0.00365596	161
11	2540.034	780.640676	154
12	2540.034	899.774282	156
13	1000.000	1673739.91	140
14	1000.000	1673740.02	162
15	1031.249	1638600.76	144
16	2205.987	88755.8553	169
17	1009.929	1660079.89	153
18	1000.464	1673008.16	149
19	2540.034	1403.02205	164
20	1206.514	1534933.98	162
21	2540.034	7138.21136	165
22	2540.034	0.00004374	169
23	2540.034	0.37952949	159
24	2540.034	4218.68781	166
25	2540.034	114146.134	165
26	2540.034	75320.4101	166
27	2540.034	662120.500	170
28	2540.034	0.01016712	165
29	2540.034	0.01770426	167
30	2540.034	0.00000011	175
31	2540.034	0.00000000	177
32	2540.034	0.00000000	177

Fig 26. Results of the Scanning on Species for Example 3

Appendix B: Chemical Mechanisms

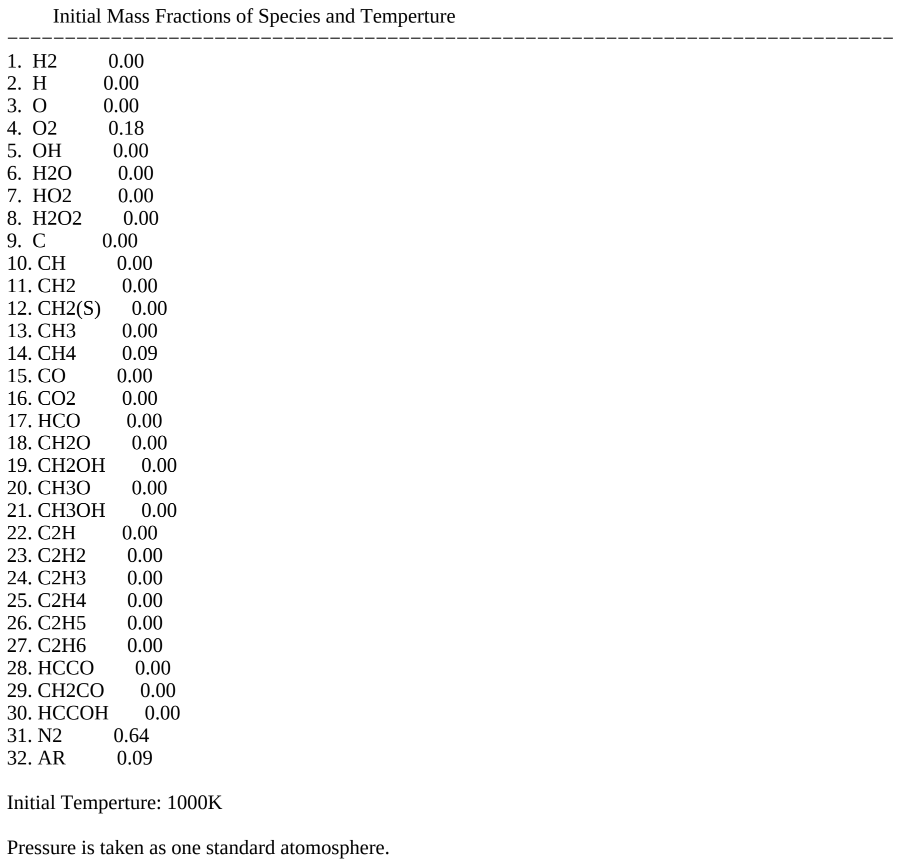
```
                 −−−−−−−−−−−−−−−−−−−−−−
                 ELEMENTS     ATOMIC
                 CONSIDERED   WEIGHT
                 −−−−−−−−−−−−−−−−−−−−−−
                  1. O       15.9994
                 −−−−−−−−−−−−−−−−−−−−−−
−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−
                 C
               P H
               H A
               A R
SPECIES          S G  MOLECULAR  TEMPERATURE  ELEMENT COUNT
CONSIDERED         E E  WEIGHT     LOW    HIGH  O
−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−
 1. O             G  0   15.99940   300   5000   1
 2. O2            G  0   31.99880   300   5000   2
 3. O3            G  0   47.99820   300   5000   3
−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−
```

```
                                    (k = A T**b exp(−E/RT))
   REACTIONS CONSIDERED                          A        b        E

 1. O3+M=>O2+O+M                       4.31E+14    0.0    92790.0
      O2              Enhanced by   4.400E−01
      O               Enhanced by   4.400E−01
 2. O2+O+M=>O3+M                       1.20E+13    0.0    −8110.0
      O2              Enhanced by   4.400E−01
      O               Enhanced by   4.400E−01
 3. O3+O=>O2+O2                        1.14E+13    0.0    19120.0
 4. O2+O2=>O3+O                        1.19E+13    0.0   420690.0
 5. O+O+M=>O2+M                        1.38E+18   −1.0     1420.0
      O2              Enhanced by   4.400E−01
      O               Enhanced by   4.400E−01
 6. O2+M=>O+O+M                        2.75E+19   −1.0   496610.0
      O2              Enhanced by   4.400E−01
      O               Enhanced by   4.400E−01

NOTE: E units Joules/mol, A units mole−cm−sec−K

        Initial Values of Mass Fractions and Temperture
−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−−
1. O   0.0
2. O2  0.9
3. O3  0.1

Initial Temperture: 500K

Pressure is taken as one standard atomosphere.
```

Fig 34. 6-Reaction Ozone Mechanism: Example 1

```
               --------------------
               ELEMENTS     ATOMIC
               CONSIDERED   WEIGHT
               --------------------
                1. H       1.00797
                2. O       15.9994
               --------------------
-------------------------------------------------------------------------------
               C
              P H
              H A
              A R
SPECIES        S G  MOLECULAR  TEMPERATURE  ELEMENT COUNT
CONSIDERED     E E  WEIGHT     LOW    HIGH  H  O
-------------------------------------------------------------------------------
 1. H2         G 0    2.01594   300   5000  2  0
 2. H          G 0    1.00797   300   5000  1  0
 3. O2         G 0   31.99880   300   5000  0  2
 4. O          G 0   15.99940   300   5000  0  1
 5. OH         G 0   17.00737   300   5000  1  1
 6. HO2        G 0   33.00677   300   5000  1  2
 7. H2O2       G 0   34.01474   300   5000  2  2
 8. H2O        G 0   18.01534   300   5000  2  1
-------------------------------------------------------------------------------


                                      (k = A T**b exp(−E/RT))
   REACTIONS CONSIDERED                     A         b        E

 1. H2+O2=2OH                         1.70E+13    0.0    47780.0
 2. OH+H2=H2O+H                       1.17E+09    1.3     3626.0
 3. O+OH=O2+H                         4.00E+14   −0.5        0.0
 4. O+H2=OH+H                         5.06E+04    2.7     6290.0
 5. H+O2+M=HO2+M                      3.61E+17   −0.7        0.0
     H2O         Enhanced by    1.860E+01
     H2          Enhanced by    2.860E+00
 6. OH+HO2=H2O+O2                     7.50E+12    0.0        0.0
 7. H+HO2=2OH                         1.40E+14    0.0     1073.0
 8. O+HO2=O2+OH                       1.40E+13    0.0     1073.0
 9. 2OH=O+H2O                         6.00E+08    1.3        0.0
10. H+H+M=H2+M                        1.00E+18   −1.0        0.0
     H2O         Enhanced by    0.000E+00
     H2          Enhanced by    0.000E+00
11. H+H+H2=H2+H2                      9.20E+16   −0.6        0.0
12. H+H+H2O=H2+H2O                    6.00E+19   −1.2        0.0
13. H+OH+M=H2O+M                      1.60E+22   −2.0        0.0
     H2O         Enhanced by    5.000E+00
14. H+O+M=OH+M                        6.20E+16   −0.6        0.0
     H2O         Enhanced by    5.000E+00
15. O+O+M=O2+M                        1.89E+13    0.0    −1788.0
16. H+HO2=H2+O2                       1.25E+13    0.0        0.0
17. HO2+HO2=H2O2+O2                   2.00E+12    0.0        0.0
18. H2O2+M=OH+OH+M                    1.30E+17    0.0    45500.0
19. H2O2+H=HO2+H2                     1.60E+12    0.0     3800.0
20. H2O2+OH=H2O+HO2                   1.00E+13    0.0     1800.0

NOTE:  A units mole−cm−sec−K, E units cal/mole

     Initial Values of Mass Fractions and Temperture
-------------------------------------------------------------------------------
1. H2      0.12
2. H       0.00
3. O2      0.88
4. O       0.00
5. OH      0.00
6. HO2     0.00
7. H2O2    0.00
8. H2O     0.00

Initial Temperture: 1000K
-------------------------------------------------------------------------------

Pressure is taken as one standard atomosphere.
```

Fig 35. 20-Reaction Mechanism: Example 2



Initial Mass Fractions of Species and Temperture

1.	H2	0.00
2.	H	0.00
3.	O	0.00
4.	O2	0.18
5.	OH	0.00
6.	H2O	0.00
7.	HO2	0.00
8.	H2O2	0.00
9.	C	0.00
10.	CH	0.00
11.	CH2	0.00
12.	CH2(S)	0.00
13.	CH3	0.00
14.	CH4	0.09
15.	CO	0.00
16.	CO2	0.00
17.	HCO	0.00
18.	CH2O	0.00
19.	CH2OH	0.00
20.	CH3O	0.00
21.	CH3OH	0.00
22.	C2H	0.00
23.	C2H2	0.00
24.	C2H3	0.00
25.	C2H4	0.00
26.	C2H5	0.00
27.	C2H6	0.00
28.	HCCO	0.00
29.	CH2CO	0.00
30.	HCCOH	0.00
31.	N2	0.64
32.	AR	0.09

Initial Temperture: 1000K

Pressure is taken as one standard atomosphere.

Fig 36. Initial Values Used for Experiments on GRI Mechanism: Example 3